Air-Xe enrichments in Elk Hills oil field gases: role of water in migration and storage

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Abstract

Hydrocarbons from the Elk Hills Naval Petroleum Reserve (NPR#1), Bakersfield, CA, are enriched in heavy noble gases. The $^{132}Xe/^{36}Ar$ ratios are as high as ∼576 times the ratio in air and represent the largest relative Xe-enrichments ever observed in terrestrial fluids. The Xe isotopic composition is indistinguishable from air. We show that these samples cannot be explained by equilibration of oil with air saturated water and secondary enrichment via a Rayleigh distillation gas stripping process. Based on laboratory studies of others with potential petroleum source rocks, we believe the source of this enriched heavy noble gas component was adsorbed air initially trapped in/on the source rocks that was expelled and mixed with the hydrocarbons during expulsion and primary migration. Kr and Xe enrichments decrease with increasing ^{36}Ar concentration. We propose a model in which an initial Kr–Xe-enriched hydrocarbon becomes diluted with noble gases extracted from air saturated groundwater during expulsion, migration, and storage. The model generates an integrated water/hydrocarbon ratio for the production fluid which indicates a minimal role for water in hydrocarbon expulsion and migration. The results are interpreted to provide time/geometrical constraints on the mechanisms by which hydrocarbons can migrate as a separate phase. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Water and brines are often co-produced with hydrocarbons, yet their role in hydrocarbon formation, migration, and accumulation is not well understood. Groundwater, meteoric or connate, tends to be saturated in air noble gases that can be readily identified by their elemental and isotopic compositions. Since noble gases associated with hydrocarbons [1–8] have isotopic compositions suggesting that air

saturated waters (ASW) play an important role in hydrocarbon systems, noble gas isotope applications to hydrocarbon processes (e.g. [2–8]) have focused on the accumulation of noble gases through water–hydrocarbon interactions.

On the assumption that hydrocarbons initially do not contain air-derived noble gases, Bosch and Mazor [2] proposed a model in which the noble gas abundance patterns in hydrocarbon systems are determined by equilibrium solubility partitioning between air-saturated water, oil, and gas. Because of the different solubilities of noble gases in oil and

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water [9,11,11,12], this mechanism can generate extremely fractionated relative abundance patterns which are similar to those observed in oil and gas fields [2–8]. However, extreme fractionation in relative abundances requires Rayleigh type distillation between water or oil and gas and is accomplished at the expense of absolute gas concentration in the residual oil or water phase. In some cases where the appropriate data exists, the absolute noble gas concentrations are inconsistent with the highly fractionated Kr/Xe/Ar ratios [2,4]. An alternative hypothesis suggests that the excess heavy noble gases associated with hydrocarbons were originally trapped in carbon-rich sediments and are, therefore, related to hydrocarbon formation and expulsion [4]. The basis of this hypothesis is the observation that carbon-rich sediments (e.g. shales) strongly adsorb noble gases [13] and are enriched in air derived Kr–Xe relative to their proportions in air or ASW [13,14,14,16].

It is important to identify the source and cause of the Kr–Xe enrichment associated with hydrocarbons to understand the role of water in hydrocarbon systems. Once the mechanisms of groundwater–hydrocarbon interaction are identified, noble gases in hydrocarbons may also be used to constrain the hydrogeologic time frame for hydrocarbon formation, migration, and storage using radiogenically and nucleogenically produced noble gases, as well as other processes, as has been done with groundwater systems (e.g., [5,7,17,18]. In this study, we report analyses of noble gases associated with oil and gas from the Elk Hills, Cymric-McKittrick, and North Coles Levee oil fields in the southern San Joaquin Valley, California, USA. We found that the production fluids are strongly enriched in Kr and Xe relative to the other air-derived noble gases (Ne and Ar), the degree of enrichment when combined with absolute gas concentration is inconsistent with the Bosch–Mazor solubility model [2], and that the magnitude of the enrichments decrease with increasing ^{36}Ar concentration. We present a model in which a Kr–Xe-enriched hydrocarbon phase becomes diluted with noble gases extracted from ASW during hydrocarbon expulsion, migration, and storage. We use the model to constrain the potential processes involved in hydrocarbon migration and storage in reservoir rock.

2. Study site

The Elk Hills oil field of the southern San Joaquin Valley (Figs. 1 and 2) is located ∼30 km southeast of Bakersfield, California, USA and is one of several giant oil fields in this region, including Midway Sunset and Kern River. President Taft established the Elk Hills Naval Petroleum Reserve #1 (NPR#1) in 1912 and production to date from the Elk Hills anticline has exceeded 2 billion barrels of oil from five producing intervals. In descending stratigraphic order, the intervals are the (1) Dry Gas Zone (Mya; 2–5 Myr), (2) Shallow Oil Zone (SOZ; 5–8 Myr), (3) Stevens Oil Zone (Stevens and Antelope; 10–12 Myr), (4) Carneros Oil Zone (Foraminite and Carneros; 20–22 Myr) and (5) Santos Oil Zone (Phacoides; 30–35 Myr, and Point of Rocks; 45 Myr) [19].

The sedimentary history of the region [19,20] is controlled principally by tectonism. A forearc basin system that existed through Mesozoic and early Tertiary time was highly modified by the subduction of the Farallon Plate under the North American Plate and the initiation of right lateral slip along the San Andreas Fault. The continental shelf to bathyl environment of the Paleocene gave way to a deep semi-enclosed basin by Oligocene time (30 Myr) which created ideal conditions for high productivity and preservation of organic material. This semi-enclosed deep basin existed through Pliocene time and concurrent uplift and lateral movement along the San Andreas Fault produced interlayered sand turbidites and organic-rich sedimentary units providing abundant source rocks and sandstone migration pathways for gas and oil.

Samples for this study were obtained from Elk Hills production wells operated by Bechtel Petroleum Operations (DOE operator for NPR#1), Cymric-McKittrick production wells operated by Chevron, and North Coles Levee production wells operated by Arco (see Fig. 2). Most of the deeper producing units (Carneros, Phacoides, Point of Rocks) are located in the WNW but the Stevens Zone covers the entire 28×12 km extent of the anticline and is the main producer. The Shallow Oil Zone samples were obtained from the central region of NPR#1.
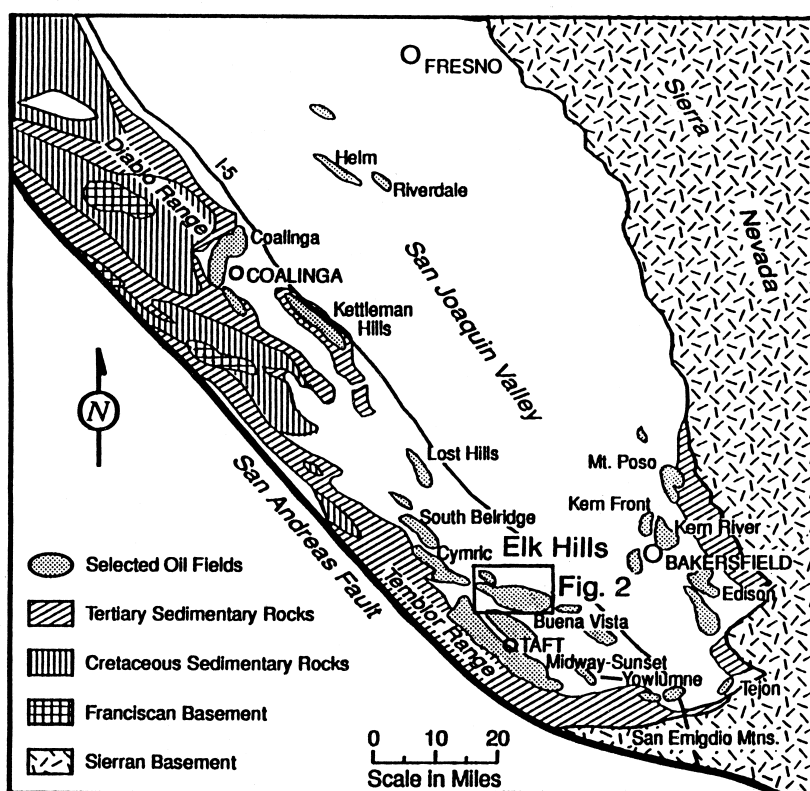
Fig. 1. Map of Elk Hills and surroundings from [29].

3. Experimental procedures

Samples for noble gas analyses were obtained from individual production wells that were allowed to flow through a high pressure liquid–gas separator for several hours prior to sampling thus ensuring that samples were from individual wells and not a mixture of wells typically served by the separator. The separators typically operate at pressures of 50–100 psig and temperatures >100°C although not all gauges were operational on all separators. The gas samples were taken in pre-evacuated high pressure Whitey cylinders fitted with valves at each end for flow through sampling. Each sample container was flushed several times with well gas to minimize air contamination.

The partitioning of noble gas from the oil/water phase to the gas phase is a function of the solubility in oil/water which, among other things, is a function of atomic mass and therefore some fractionation

might occur in the separator. Ballentine et al. [7] found 96–82% of the He–Ne–Ar fraction was transferred to the gas phase at the separator confirming both the strong partitioning into the gas phase as well as minimal fractionation of the noble gases via solubility effects. The very high gas/(water + oil) volume ratios (Table 1) for the Elk Hills wells (10^3–10^5) suggests that the noble gases will be nearly completely partitioned into the gas phase. Therefore, we have assumed that the noble gas ratios measured in this study represent the of sum of the downhole (reservoir) concentrations. In any case, noble gas solubilities and the results of [7] suggest that the measured values may represent minimum estimates of the degree of Kr and Xe enrichment. This effect will strengthen the arguments made below.

Noble gas analyses were performed in the RARGA laboratory of the Lawrence Berkeley National Laboratory, University of California. The RARGA lab consists of an all-metal gas purifica-
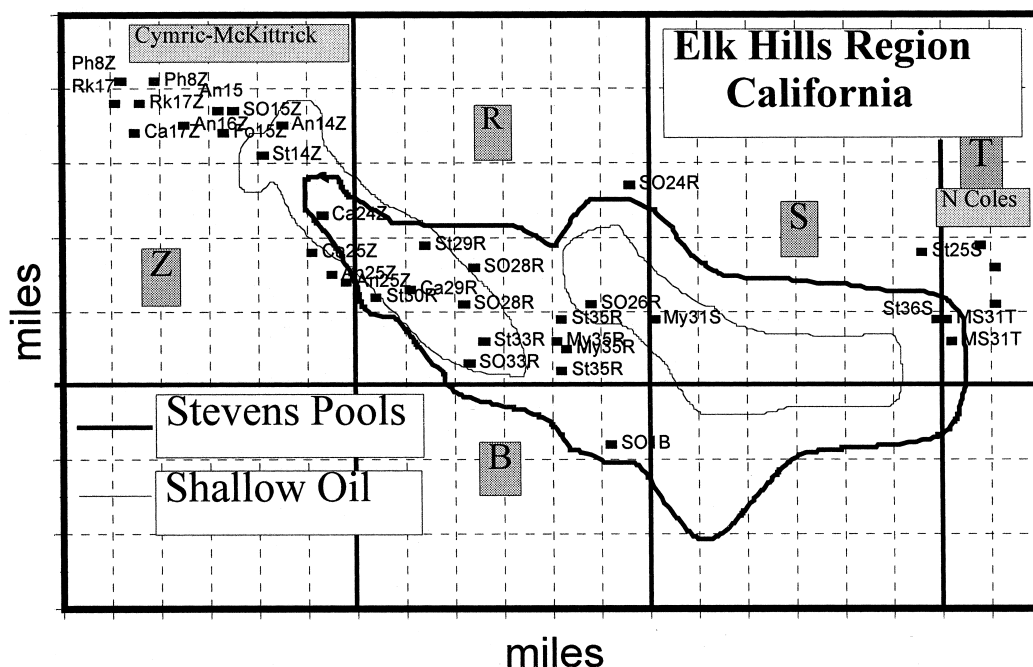
Fig. 2. Locations of wells within the Elk Hills anticline.

tion line, designed specifically for routine reactive gas cleanup and noble gas elemental and isotopic analyses of dirty fluid samples. Details of the sample purification and analytical procedures for petroleum samples have been published elsewhere [4,21].

4. Results and discussion

Noble gas abundances are given in Table 1 as F values for a specific noble gas isotope, ^nNg defined as:

$$F(^nNg) = \frac{[^nNg]/[^{36}Ar]_{sample}}{[^nNg]/[^{36}Ar]_{air}} \quad (1)$$

$F(^nNg)$ values for water and oil in equilibrium with air at 20°C are also given for reference. Concentrations of ^{36}Ar in the hydrocarbon samples are given in cm^3 STP/$cm^3_{total\ gas}$. Production records from Bechtel Petroleum indicate that total gas in the production stream is typically 70–80% methane with 7–10% carbon dioxide and 10–20% ethane plus propane with less than 4% contributions from trace amounts of N_2 and other gases. In Table 1, we also in-

clude the concentrations of ^{36}Ar per gram-carbon (cm^3 STP/g_C) assuming a gas composition of 100% methane plus trace amounts of noble gases.

We have chosen to normalize the data to g_C because it represents the common basis among the source rock, the liquid hydrocarbon and the gas (methane). We have reconstructed the hypothetical distribution of rare gases among the gas/oil/water (G/O/W) phases at the temperature and pressure at depth and found that $\gg$90% of the noble gas is in the gas phase for all samples. However, we recognize that the production ratios of G/O/W do not represent true conditions in situ because the G/O/W production ratios are modified from the in situ G/O/W ratio by the relative flow of the three phases and the perforation intervals relative to the G/O and O/W boundaries. It could be argued that the calculated concentration per g_C based on methane does not represent the concentration per g_C in situ because such a calculation does not include the carbon in the oil phase. However, because of the very large gas/(oil + water) ratios of the sampled wells, including such a 'correction' would not change our interpretation below. More importantly, such a correction may not

be appropriate. The important relation is that kerogen produces 0.1–0.4 g_C as CH_4 for every 1 g_C as oil [22,23]. Since conditions in situ require more that $\gg$90% transfer to the gas phase, the most we can be in error by calculating concentration per g_C from the methane as a proxy for $g_{C\text{-total}}$ is a factor of 1/0.4 to 1/0.1 (e.g., 2–10×). Thus, while the gas phase concentrations reported here can be shown to approximate the sum of water + oil + methane noble gases, the hydrogeologically unknown relations (at depth) among these three phases preclude assignation of a specific noble gas fraction to each separate phase. Nonetheless, the noble gas concentration in the separated methane phase represents a good estimate (within 2–10×) of the noble gas concentration per gram carbon in the total phases.

The isotopic compositions of the individual noble gases in the southern San Joaquin oil fields (to be reported elsewhere) are consistent with an ASW and/or air source with the exception of excess ^{4}He and excess ^{40}Ar. The increasing enrichment of noble gas as a function of atomic number [$F(^{22}$Ne) $< F(^{84}$Kr) $< F(^{132}$Xe)] observed in this study is consistent with previous studies [2,4,6] and with an ASW influence on the air-derived noble gas inventory. However, the average Xe enrichment factors ($F(^{132}$Xe)) are ~30 times the air ratio and as high as 576 times the air ratio in the Shallow Oil Zone (SOZ). These represent the highest ^{132}Xe/^{36}Ar ratios measured in terrestrial fluids.

In Fig. 3, we show the possible $F(^{132}$Xe) enrichment of a gas phase in contact with oil–water
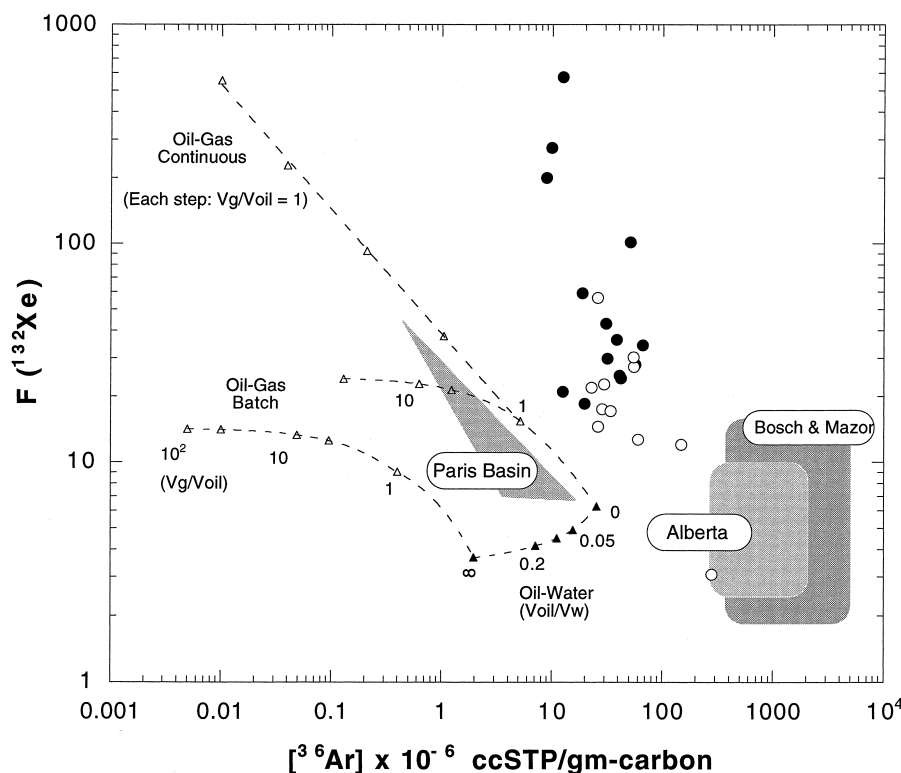

Fig. 3. $F(^{132}$Xe) vs. ^{36}Ar relations for various scenarios. The dashed lines represent the evolution of the noble gas composition of gas following a batch or continuous distillation from an initial equilibrated oil–water mixture. The compositions were calculated following the model of Bosch and Mazor [2] and their potential range of modification by Rayleigh distillation processes [21]. Data from petroleum wells in the Elk Hills and North Coles Levee Fields (filled circles) and Cymric-McKittrick Field (open circles) cannot be produced by oil equilibration with ASW and/or secondary distillation and enrichment processes. The Alberta gas fields [6] and the data of Bosch and Mazor [2] also cannot be produced by oil–ASW equilibration or secondary enrichment. On the other hand, the Paris Basin fluids [5] may have been completely stripped of an initial source rock $F(^{132}$Xe) signature followed by a re-equilibration with ASW.

Table 1
Elk Hills NPR#1 noble gas data

Sample	Location well #	Formation	Label	Depth (ft, avg)	Water/oil (l/l)	Gas/oil (l/l)	^{36}Ar (10^{-8} cm^3/cm^3)	^{36}Ar/g$_C$ (10^{-6} cm^3/g$_C$)	$F(^4$He)	+/−
SJQ95-10	452-35R	IV Mya	My35R	−2087	gas only	gas only	2.25	42.1	1833	111
SJQ95-12	28-28R	SOZ, Wilhelm-2	SO28R1	−2575	4.90	856	0.48	8.9	1790	109
SJQ96-03	64-24r	SOZ, submulina	SO24R	−2975	2.30	33	0.67	12.5	1819	111
SJQ96-07	66-28r	SOZ, W1	SO28R	−2637	4.00	1231	0.53	9.9	4477	276
SJQ95-25	356-15Z	Etchigoin (SOZ)	SO15Z	−2257	gas only	gas only	7.96	149	956	58
SJQ95-22	312-16Z	Antelope	An16Z	−4232	1.25	1127	1.39	26.0	1014	62
SJQ95-13	5-344-14Z	Stev?Ant	An14Z	−5457	9.70	2600	2.07	38.6	4514	274
SJQ96-11	12-29	21-1 U Stevens	US29T				0.10	1.8	635	39
SJQ95-26	376A-15Z	Antelope	An15Z	−4921	24.00	5340	1.83	34.1	785	48
SJQ95-27	323X-25Z	Antelope	An25Z1	−5808	6.10	3433	2.96	55.2	3072	188
SJQ95-28	327-25Z	Antelope	An25Z	−6096	51.00	6433	2.92	54.4	3132	191
SJQ95-15	352-33R	Stevens A	St33R	−5500	4.50	5343	1.70	31.8	832	50
SJQ96-08	17-14z	Stevens A	St14Z	−6120	7.00	6926	2.20	41.0	3124	189
SJQ95-07	318-30R	Stevens AB	St30R	−6318	6.30	2800	3.04	56.7	2623	159
SJQ95-09	326-35R	Stevens	St35R	−6432	4.00	667	1.66	30.9	854	52
SJQ95-16	381-36S	Stevens	St36S	−8867	1.00	28000	3.57	66.7	1373	83
SJQ95-17	361-25S	Stevens	St25S	−9699	0.05	30000	2.75	51.3	1220	74
SJQ95-08	343-29R	Stevens D	St29R	−6013	17.70	316	1.01	18.8	1404	85
SJQ95-24	545-15Z	Foraminite	Fo15Z	−6606	1.20	2375	1.41	26.2	1010	61
SJQ95-23	574X-17Z	Carneros	Ca17Z	−6257	16.00	890	1.22	22.8	1851	112
SJQ95-29	533-25Z	Carneros	Ca25Z	−9112	2.20	877	1.59	29.6	887	54
SJQ95-11	578-24Z	Carneros	Ca24Z	−9381	2.00	2323	1.06	19.7	1534	93
SJQ95-14	515-29R	Carneros	Ca29R	−9213	4.00	21370	0.67	12.6	2329	141
SJQ95-21	87X-8Z	Phacoides	Ph8Z	−8202	2.40	198	1.54	28.8	908	55
SJQ95-19	58X-8Z	Phacoides	Ph8Za	−8233	1.40	505	15.06	281	167	10
SJQ95-18	711-17Z	Point of Rocks	Rk17Z1	−9056	0.02	196	3.23	60.2	437	26
20ºC air saturated water								1.07	0.26	
20ºC air saturated 600 mmolar NaCl water								0.87	0.27	

mixture using both batch and continuous Rayleigh distillation processes. The compositions are calculated following the model of [2] (using the solubility data of [10,12]) and represent the range of possible values for a hydrocarbon system in which ASW is the only air-derived noble gas source. In Fig. 4, we show the effect of these processes on $F(^{84}$Kr). It is clear that the ^{36}Ar concentrations and the $F(^{132}$Xe) and $F(^{84}$Kr) enrichments of the Elk Hills samples are inconsistent with the Bosch–Mazor model [2] and, therefore, the Elk Hills hydrocarbons require a Xe and Kr source other than or in addition to ASW. Since the elemental isotopic composition of this enriched source is indistinguishable from air, we suggest that this Kr–Xe-enriched component originated as an adsorbed/trapped component in the carbon-rich hydrocarbon source rocks as suggested by [4] and supported by noble gases measured in carbon-rich sedimentary rocks [13–16].

From Fig. 3, it is clear that the data of [2,4] are also not consistent with a model in which ASW is the only noble gas source. On the other hand, the oils of the Paris Basin [6] are consistent with Bosch–Mazor model [2] and may have evolved by equilibration between ASW, oil, and gas. This implies that either the Paris Basin oils did not contain the additional hydrocarbon associated noble gas component, or that this component was lost from the hydrocarbon phase prior to equilibration with ASW.

Noble gases extracted from ancient and modern carbon-rich sediments (Fig. 5) are enriched in Kr–Xe in comparison to their proportions in air: ^{132}Xe/^{36}Ar ratios vary from ∼10–10^4 [14–16]. The general pattern of noble gas enrichment (Xe > Kr > Ar) suggests adsorption or a similar process which preferentially selects the larger-heavier noble gases. In laboratory vacuum-heating experiments, the heavy noble gas enriched component is released at temperatures in excess of ∼850ºC, suggesting a secondary

$F(^{22}Ne)$	+/-	$F(^{84}Kr)$	+/-	$F(^{132}Xe)$	+/-	H_2O/C (g/g)	$F(^{132}Xe)_{init}$		$F(^{84}Kr)_{init}$	
							^{22}Ne base	^{36}Ar base	^{22}Ne base	^{36}Ar base
0.719	0.059	4.58	0.11	24.2	1.4	<40		2602		341
0.301	0.019	25.96	0.52	199.9	10.9	<9	4781		584	
0.560	0.048	58.54	1.17	576.0	31.4	<12		9482		934
–	0.260	38.89	1.02	274.6	15.2	<10	12216		1658	
0.733	0.025	3.92	0.08	12.0	0.7	<139		1431		340
0.313	0.027	5.94	0.12	56.5	3.1	<25	3966		306	
0.120	0.052	6.37	0.13	36.3	2.0	<15	58		9	
0.520	0.138	3.62	0.11	25.8	1.9	<2		58		6
0.542	0.016	3.37	0.07	17.2	0.9	<31		244		28
0.261	0.052	4.36	0.10	27.3	1.5	<45	168		19	
0.129	0.038	4.66	0.10	30.2	1.7	<22	50		7	
0.203	0.009	5.04	0.10	29.8	1.6	<20	77		11	
0.193	0.008	4.99	0.10	24.9	1.4	<25	62		10	
0.413	0.013	4.51	0.09	27.9	1.5	<53		1348		147
0.164	0.009	5.77	0.12	43.0	2.3	<16	86		10	
0.042	0.039	4.77	0.10	34.4	1.9	<8	39		5	
0.315	0.012	11.19	0.22	101.6	5.5	<47	5054		479	
0.164	0.015	6.80	0.14	59.3	3.2	<10	119		12	
0.313	0.013	2.98	0.06	14.5	0.8	<25	526		55	
0.223	0.026	3.73	0.07	22.0	1.2	<16	67		8	
0.262	0.024	3.79	0.08	22.6	1.2	<24	119		13	
0.145	0.038	3.28	0.07	18.5	1.0	<9	30		4	
0.324	0.045	3.75	0.08	21.0	1.2	<12	275		31	
0.719	0.022	2.51	0.05	17.5	1.0	<27		444		23
0.926	0.026	1.20	0.03	3.1	0.2	<27		3		1
0.134	0.006	2.92	0.06	12.7	0.7	<25	20		4	
0.31		1.84		3.3						
0.32		1.82		1.82						

trapping mechanism that enables the carbon-rich sediments to retain the heavy noble gas component over geologic time [14–16]. However, the specific trapping sites and mechanisms have not been defined. One possibility involves organics as potential sorption/trapping sites. For instance, large enrichments of heavy noble gases were found in thucolite, a Th–U-organic-rich mineral closely associated with the presence of petroleum [16]. Further evidence for an association with source rock carbon and for a secondary trapping mechanism was found by chemically isolating a carbon-rich phase from 3.4 Byr old kerogen-rich cherts that released a Xe-enriched component at laboratory temperatures of 1000ºC [16]. It was concluded that carbon was the carrier phase for excess Xe.

Oil formation occurs at temperatures of 50–250ºC [22] causing a significant alteration of the kerogen source material as it evolves to expelled methane–alkane and residual bitumen fractions. Such a radical alteration of the organic structure in the sediments could break the sites in which the heavy noble gas component is adsorbed and trapped, thus releasing this enriched component to the expelled methane–oil phase during primary migration.

5. Water–oil mixing model

The $F(^{132}Xe)$ values (e.g. Fig. 3) of ~30–580 strongly suggest the influence of a second adsorbed and trapped noble gas component which, must also be air-derived. Support for a second air-like noble gas component is provided by (1) co-variations in the degree of Kr and Xe enrichment (Fig. 4) which are consistent with mixing between a heavy noble gas enriched component, like that observed in carbon-rich sediments (e.g. [16]) and ASW [$F(^{132}Xe)$ ~ 3] (dash–dot line) and/or air and (2) the decrease in $F(^{132}Xe)$ with increasing concentrations of ^{36}Ar
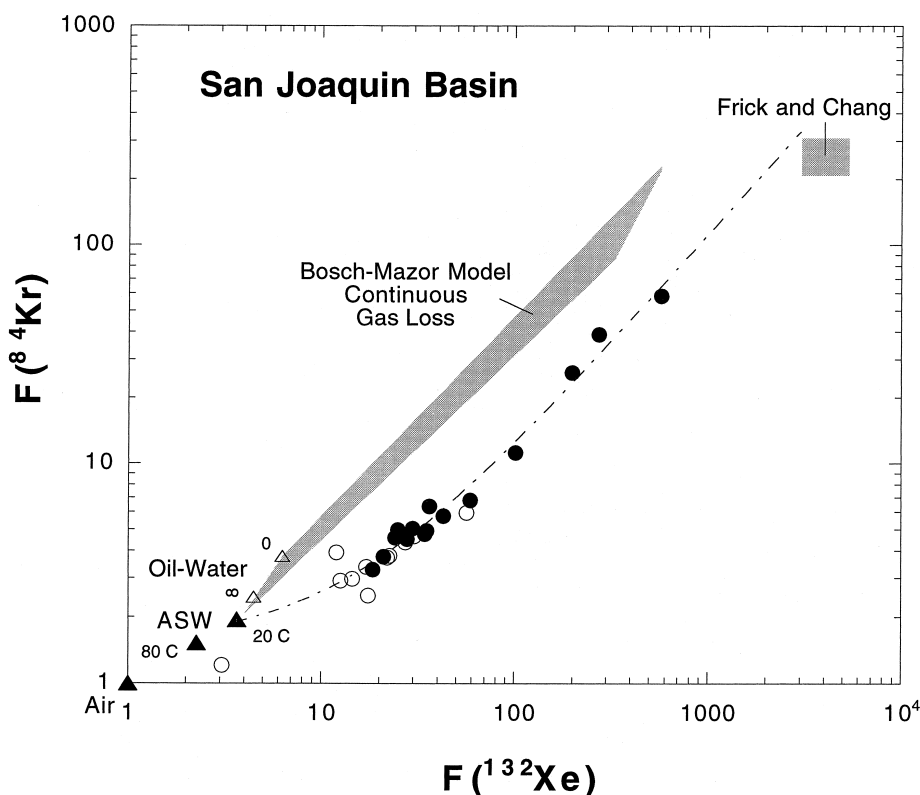
Fig. 4. The Kr/Ar and Xe/Ar ratios in Elk Hills oil wells. The data symbols (open and filled circles) are the same as in Fig. 3. Filled triangles represent the composition of air and groundwater in equilibrium with air (ASW) at 10 and 80°C. The open triangles and adjoining shaded region depict the range in values predicted by the Bosch–Mazor model shown Fig. 3. The dash–dot mixing line is constructed from a weighted least squares fit to the data set that was forced through 20°C ASW. The shaded box labeled reflects the noble gas composition of carbon-rich extracts from cherts as measured by Frick and Chang [16].

(Fig. 3), as would be expected if ASW were diluting the initial hydrocarbon air-like noble gas component. We propose that the first (Xe-enriched) component is liberated from the source rock during expulsion and primary migration and that the second component is acquired during secondary migration and reservoir storage as the hydrocarbon phase interacts with ASW from which noble gases are extracted, diluting the initial heavy noble gas enriched signature.

The contributions to the inventory of ^{132}Xe, ^{84}Kr, ^{36}Ar, and ^{22}Ne in the system can be expressed by the generalized formula:

$$[^{n}Ng]_{total} = {}^{n}Ng_{kerogen\text{-}initial} + B({}^{n}Ng_{ASW}) + {}^{n}Ng_{air}$$
$$(2)$$

where kerogen-initial accounts for the noble gas component exsolved with the hydrocarbons dur-

ing formation, ASW refers to the air saturated groundwater component diluting the hydrocarbon end member, B is the water/hydrocarbon mass ratio (g_{H_2O}/g_C), and air reflects the potential for air contamination during sampling or subsequent processing.

Ne has a low solubility in oil and water and, therefore, the Ne contents in the samples are low and more susceptible to and indicative of air contamination. However, the $F(^{22}Ne)$ data are more difficult to interpret because it is unclear whether the Ne which accompanies the Kr–Xe enriched in the hydrocarbon phase is enriched ($F(^{22}Ne) > 1$) or depleted ($F(^{22}Ne) < 0.3$, 20C ASW). Both conditions have been observed in the source rocks measured in the lab (Table 2; [14–16]). It should also be noted that the relative enrichment in air Ne on the original
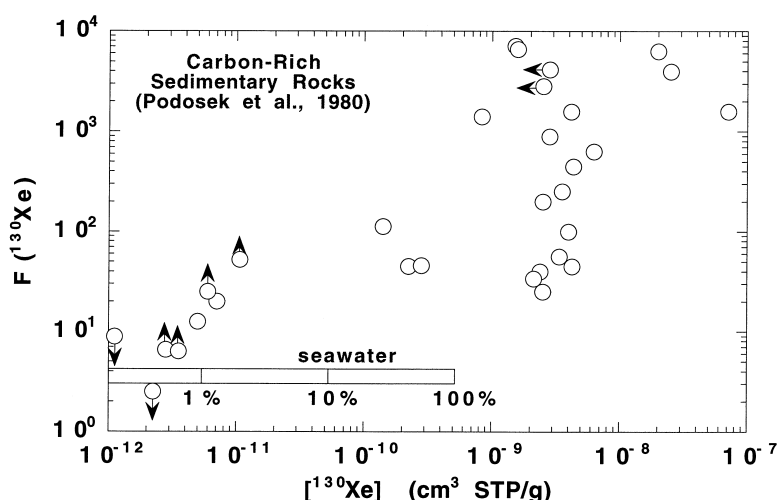
Fig. 5. Summary of Xe/Ar and Xe abundances in carbon-rich sedimentary rocks (e.g. shales) reproduced from Podosek et al. [14]. The seawater line indicates the composition that would be expected if all the noble gases in the sediments were accounted for by trapped seawater; the percentages would correspond to the fraction of water in the rock.

source rock does not preclude the observation of isotopically enriched Ne (as excess ^{21}Ne and excess ^{22}Ne) due to nucleogenic processes in situ (e.g., [3,7]), although the greater the $F(^{22}$Ne) the less discernable will be the excesses of ^{21}Ne and ^{22}Ne that can be observed.

A comparison of the $F(^{22}$Ne) and $F(^{132}$Xe) data (Fig. 6) suggests that most of the data are consistent with the dilution model of this study (solid lines), which invokes mixing between 20ºC ASW and an $F(^{132}$Xe) enriched component. It is also evident from Fig. 6 that there must be at least two different Xe-enriched components; one with $F(^{132}$Xe) $\sim$ 50 and $F(^{22}$Ne) $\sim$ 0.0 and the other with $F(^{132}$Xe) > 576 and $F(^{22}$Ne) $\geq$ 0.3. Additionally, several

samples with $F(^{22}$Ne) > 0.4 appear to contain a non-fractionated air component (samples depicted by open triangles). There is no evidence or reason to believe that this air component is indigenous to the reservoir gas and it is more likely to be an air contaminant introduced during sampling. There are several potential opportunities for contamination: (1) the sample cylinders may either leak air or could have been improperly evacuated prior to sampling, although analyses of sample cylinder blanks indicate otherwise; (2) flow of gas and oil through the well bore may entrain air leaking through the casing or at casing flanges; or (3) air leaks into the oil–gas separators. Since the separators are not designed to be vacuum tight, contamination is likely, especially

Table 2
Source rock compositions

Reference [a]	$F(^{22}$Ne)	$F(^{84}$Kr)	$F(^{132}$Xe)	$[^{36}$Ar] $\times 10^{-8}$ cm^3 STP/g	$[^{36}$Ar] $\times 10^{-8}$ cm^3 STP/g$_C$
Bogard et al. [15]	4.6–1010	0.7–1145	1600–45000	0.15–45	3–2000 [b,e]
Frick & Chang [16]	7.6–15.6	220–261	2955–4345	n.a.	8–20 [c,e]
Podosek et al. [14]	0.1–11.3	0.8–20.5	4–1300	0.1–1.0	30–500 [d,e]
This work	n.a.	4–1658	30–12216	n.a.	0.2–25300

[a] Data sources are [14–16] and this work calculated from the measured ^{22}Ne and ^{36}Ar compositions as described in the text. [b] Data are for thucolites. [c] Data are for chemically isolated C fractions, and for thucolite and shales. [d] Data are for shales. [e] For all calculations, (a) thucolites are assumed to be 65%C [28]; and (b) shales are assumed to be 0.05 g$_C$/g$_{rock}$ with a 4–7% conversion of total carbon to carbon as methane [22].
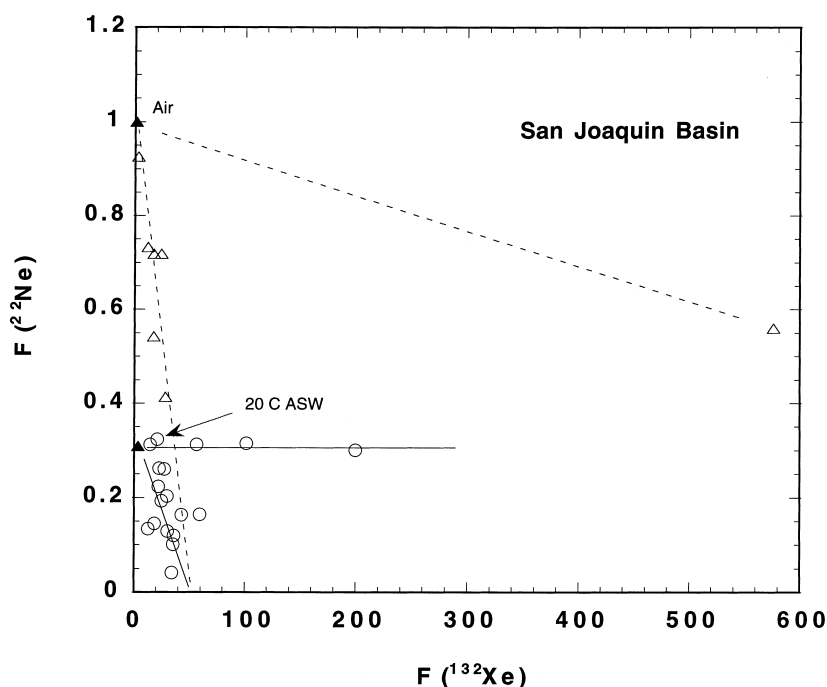
Fig. 6. The $F(^{22}Ne)$ and $F(^{132}Xe)$ ratios in Elk Hills oil wells. The triangles represent samples that appear to have been compromised by atmospheric contamination as indicated by the dashed lines. The solid lines represent hypothetical mixing lines between 20C air saturated water (ASW) and components enriched in Xe. Despite the possibility of air contamination, the data distribution requires at least two Xe-enriched components.

for samples collected at low pressure and low flow rate through the separator.

Even though some samples show evidence for air contamination, if air contamination is assumed to be negligible for most of the samples, then limits on the composition defined as kerogen-initial can be estimated from the equation above by iterative subtraction of ASW (20°C). This results in an estimate of the maximum value for the water/carbon mass ratio, $B = 8–60 \ g_{H_2O}/g_C$. (This value is constrained by the absolute amount of ^{36}Ar and/or ^{22}Ne in the sample and is similar to calculations by others [7]. The difference is that the initial concentration of noble gases in the hydrocarbon phase was assumed to be zero [7], whereas we have shown that the initial concentration of ^{36}Ar in the hydrocarbon is small ($<10^{-7}$ cm^3 STP $^{36}Ar/g_C$ [14–16]) compared to ASW but that the heavy noble gases are distinctively enriched in this initial expulsion of the hydrocarbon).

To compare the ^{36}Ar concentrations in the Elk Hills wells to concentrations measured in potential

source rocks [14–16], we normalize the noble gas concentrations to the carbon (cm^3 STP/g_C) in the samples. The carbon normalized ^{36}Ar concentrations for the wells are given in Table 1. If we assume that (1) the noble gas content in carbon-rich sediments measured in the laboratory are representative of petroleum source rocks and (2) all of the heavy noble gas component is released to the hydrocarbon phase during generation and expulsion, then the concentration of noble gas per gram carbon in the expelled phase can be reasonably estimated. These estimates, as well as, the Xe-enrichment factors in the carbon-rich rocks and the results of the iterative subtraction of the ASW component are summarized in Table 2 and are shown in Fig. 7 as a range of values in the upper left of the figure. The solid lines in the figure are dilution trajectories depicting the effect of non-equilibrium addition of ASW noble gases extracted from groundwater. The numbers along each trajectory are example water/carbon mass ratios, B in g_{H_2O}/g_C. In general, the composi-
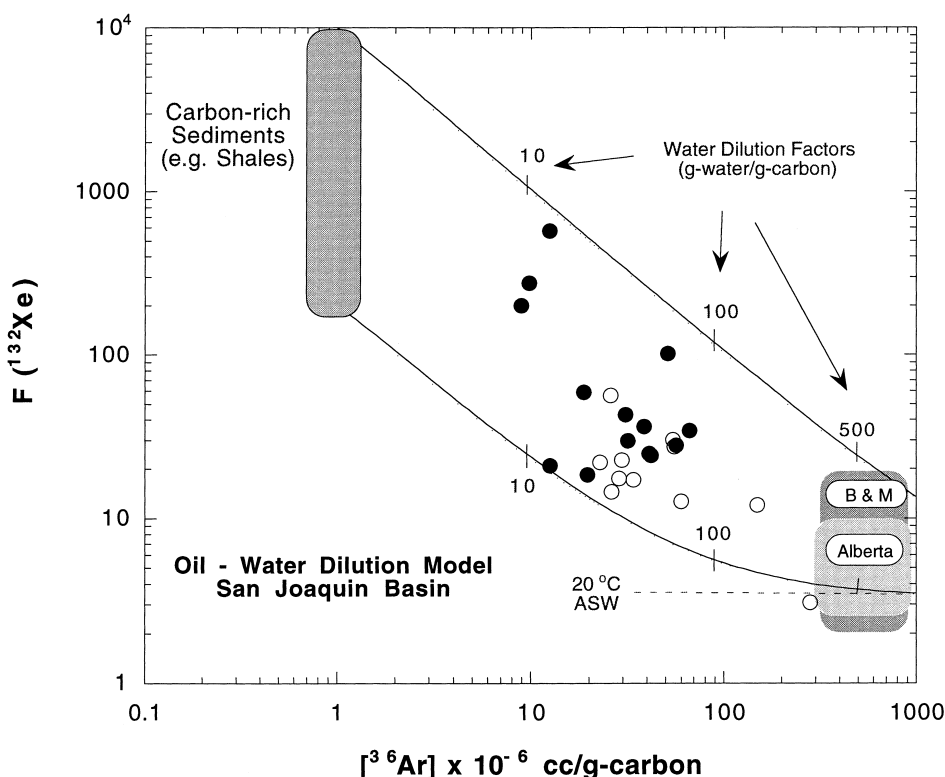
Fig. 7. The oil–water dilution model. The data symbols (filled and open circles) are the same as in Fig. 3. The shaded region covers the range of noble gas compositions measured in carbon-rich sedimentary rocks with the highest degree of Xe-enrichment (Fig. 2) and represents the assumed initial hydrocarbon compositions (kerogen-initial). The solid lines are dilution trajectories depicting the change in noble gas composition of oil as it quantitatively extracts noble gases from the ASW. If the extraction of noble gases from the ASW phase to the hydrocarbon phase is governed by equilibrium solubilities, then the asymptote for $F(^{132}Xe)$ at high ^{36}Ar concentrations will be closer to $F(^{132}Xe) = 10$ and the values of g_{H_2O}/g_C will be slight underestimates because of the noble gases left in the ASW phase. These simplifications do not change the results of this study.

tion of the Elk Hills production fluids conform to the simple model and suggest that during hydrocarbon expulsion, migration, and storage each gram of carbon has equilibrated with only ~10–100 g of ASW. For comparison, the data of [2,4] have much lower $F(^{132}Xe)$ (Fig. 7) and higher ^{36}Ar concentrations consistent with $B =\sim 200$–1000 g_{H_2O}/g_C.

The low integrated water/carbon ratios (<100 g_{H_2O}/g_C) calculated for the Elk Hills hydrocarbons, imply that hydrocarbon expulsion and migration in environments with very low water/oil ratios can produce large accumulations; Elk Hills has produced over 2 billion barrels of oil since 1910. Therefore, any mechanism invoked to explain migration must include interaction with groundwater that is consistent with these low ratios. Two possible scenarios

have been cited: (1) dissolution and migration in an aqueous phase [22] and (2) expulsion and migration as a separate oil or oil-dissolved-in-super-critical-methane phase [23]. Little credence is given to dissolution in an aqueous phase because differential solubilities of light and heavy oil fractions (in water) would produce highly fractionated oil phases which are not observed [23]. Instead expulsion of hydrocarbon as a methane/oil mixture and migration as a separate fluid would be the favored dominate mechanism for migration [23]. However, total dissolution of oil in an aqueous phase would not fractionate the light and heavy oil fractions. The model water/oil ratios derived above can be used to test the feasibility of these two different migration mechanisms.

The solubility of oil in water is ~50–150 ppm,

by weight [24], indicating that aqueous transport of oil would require water/oil ratios in excess of $\sim 10^4$ g_{H_2O}/g_C; much greater and, therefore, inconsistent with the limits imposed by the model. Therefore, this study supports the organic geochemical argument that aqueous phase involvement in the generation, expulsion, migration, and storage of oil and gas is minimal and supports the concept of a separate organic phase (oil and/or oil dissolved in super-critical methane) migration mechanism for hydrocarbons. The driving force for migration of this distinct and separate hydrocarbon phase can be either buoyancy or (aqueous) pressure drive.

The calculation of $F(^{132}Xe)_{kerogen-initial}$, despite the inherent large uncertainties, and the data distribution (Figs. 6 and 7) require at least two different hydrocarbon end member components. Production fluids in the Elk Hills may therefore have evolved from more than one source rock. However, except for fluids from the shallow oil zone (SOZ) which have the largest Xe enrichments, there is little geographic grouping or formational separation to suggest that carbon from one type of source rock dominates in any one group of wells. Instead, the variation in noble gas compositions of the expelled hydrocarbon end members may represent spatial heterogeneity in the source rock rather than a stratigraphically distinct source rock. That such heterogeneities in noble gas initial compositions can exist in such geographic proximity combined with the very low estimated g_{H_2O}/g_C ratios further suggests that (1) the hydrocarbons migrate as separate phases and (2) accumulation reservoirs act as distinct compartments inhibiting hydrocarbon mixing and homogenization.

6. Constraints on oil migration

The rate that a separate and distinct oil phase acquires noble gases from ASW is likely to be governed by diffusion/dispersion across the phase boundary. Given an effective dispersion coefficient for water and the volume of water diffusively in contact with a specific hydrocarbon volume, water–oil exposure times for given geometries can be evaluated. Consider a well-mixed volume of oil with a characteristic length, L_C, which is perpendicular to the greatest areal extent of the organic 'slug' and,

therefore, perpendicular to the greatest area through which diffusion of noble gases from the water occurs to the oil. The contact depth from which noble gases are extracted from the water to the oil, Δz, is described by scaling the diffusion process as:

$$\Delta z = (K \cdot \Delta t)^{1/2} \tag{3}$$

where K is the diffusion/dispersion coefficient and Δt is the exposure time. The volume of water contacted by an hydrocarbon phase in time Δt is:

$$V_{H_2O} = \Delta z \cdot A \cdot \Phi = (K \cdot \Delta t)^{1/2} \cdot A \cdot \Phi \tag{4}$$

where A is the area and Φ is the porosity. Therefore the volume ratio of water to oil is:

$$\frac{V_{H_2O}}{V_C} = \frac{\Delta z \cdot A \cdot \Phi}{L_C \cdot A \cdot \Phi} = \frac{(K\Delta t)^{1/2} \cdot A \cdot \Phi}{L_C \cdot A \cdot \Phi} \tag{5}$$

Assuming, on average, an oil density of $\rho_{oil} = 0.85$ g cm^{-3}, a carbon concentration in oil of $C_C = 0.85$ g$_C$ g$_{oil}^{-1}$; and a density of the aqueous phase $\rho_{H_2O} = 1.0$ g$_{H_2O}$ cm^{-3}, this equation can be rearranged to give an expression relating the ratio B, g_{H_2O}/g_C, to time and the characteristic length scale of the system:

$$B = \frac{(K\Delta t)^{1/2} \cdot \rho_{H_2O}}{L_C \cdot \rho_{oil} \cdot C_C} \tag{6}$$

For the Elk Hills wells, the time and length scales of a diffusive/dispersive process that delivers noble gases from groundwater to the oil phase is constrained by the model calculated values for B (~ 6–80 g_{H_2O}/g_C).

Using a dispersion coefficient for noble gases in water of 10^{-5} cm^2 s^{-1} [25], Fig. 8 shows how exposure of oil to water changes B as a function of time and the characteristic scale length of the oil phase, L_C. The maximum oil–water exposure time available for the Elk Hills is <30 Myr, the age of the presumed source rocks. More realistic exposure times are likely to be shorter (~ 10–20 Myr), depending on when the source rocks passed into the oil generation window. The shaded region in Fig. 8 is defined by the calculated B ratios and the maximum duration of exposure to an aqueous phase ($t < 30$ Myr) for the Elk Hills samples. Since exposure can occur during migration and while in the reservoir, the relative importance of exposure during each stage will be determined by the respective scale lengths. During storage in the reservoir, a characteristic length scale for the storage
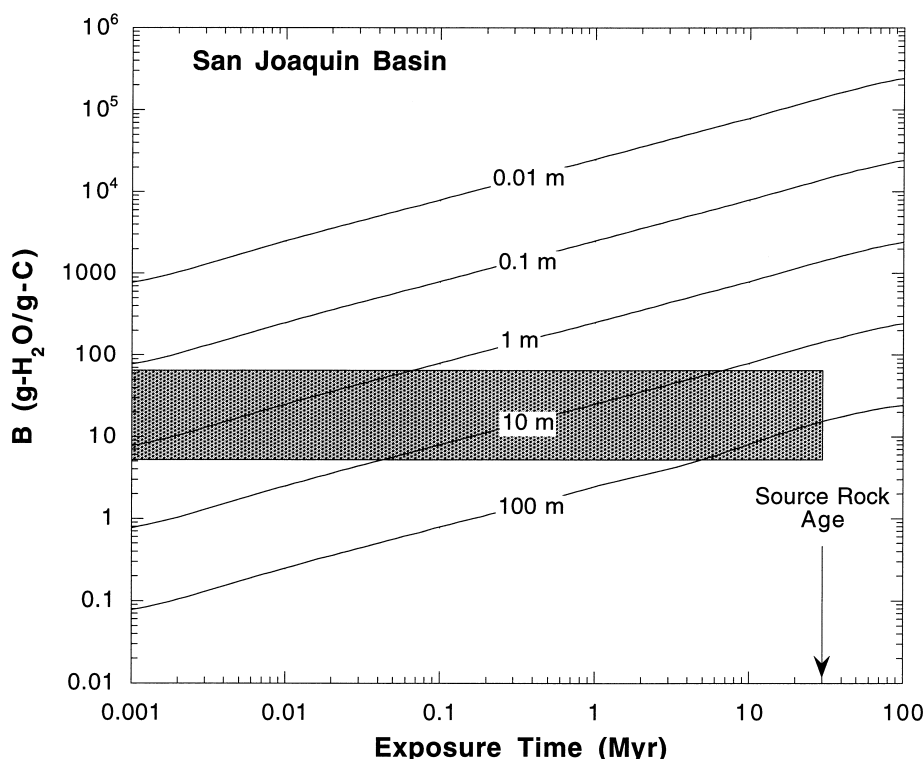
Fig. 8. The *B* values (water/carbon mass ratios) as a function of increasing time of exposure to air saturated groundwater for various characteristic length scales (L_C). The calculated range of *B* values for the Elk Hills samples and the allowable geologic limits on the exposure time are shown by the shaded region.

reservoirs of 100 m implies that, even after 30 Myr of exposure, diffusion of noble gases from an aqueous phase in contact with the reservoired oil will have little effect on the measured *B* ratio. Therefore, all or most of the dilution of initially high $F(^{132}Xe)$ by dilution with ASW must occur during migration (note that a change in the dispersion coefficient by 10× changes the calculated *B* ratio by 3.16×). *B* is thus an indicator of the time scale for migration and will depend strongly on the characteristic length scale of the hydrocarbon during migration. For the low *B* values [highest $F(^{132}Xe)$] associated with oil from the Elk Hills Shallow Oil Zone, $L_C = 10$ m allows ∼5 Myr for migration, $L_C = 1$ m scale length restricts migration times to ∼10,000 yr, and $L_C = 0.01$ m is only possible if migration times are <1 yr.

Oil will migrate as a distinct separate phase under the influence of buoyancy or groundwater pressure. Typical buoyant rise velocities imply migration rates

of ∼1–10 km/Myr, which imply that a 1 m oil 'stringer' could migrate from as short a distance as 100 m over the 10,000 years time constraint imposed by the geometrical considerations. Despite the large volume of oil that has been produced (∼2 billion barrels from Elk Hills), the very short migration distances (<100 m) implied by buoyant flow are not entirely implausible. Assuming reasonable carbon contents and oil production efficiencies, 2 billion barrels of oil could be generated from ∼30 km³ of source rock. Therefore, a ∼100 m thick block of source rock with an areal extent equivalent to the Elk Hills field (12 × 28 km) could account for all the oil produced. In this scenario, the shales that are interbedded with the high permeability sands from which the oil is produced are the source rocks. Buoyancy driven flow for a separate oil phase with a characteristic dimension of $L_C = 0.01$ m would be limited to <1 yr of migration in contact with an aqueous phase which is unlikely to allow the

extent of reservoir concentration observed. Thus, the geometry of oil migration must be of the order $L_C > 0.01$ m.

The migration of oil as a separate phase driven by groundwater pressure is likely to be at least ten times faster with migration rates of $\sim$10–100 km/Myr. This implies that a 10 m oil 'plug' (bounded between two low permeability shale horizons) can be transported by groundwater pressure from a distance of 500 km. Such large transport distances are often envisioned because typically reservoir rocks are located significantly above the oil/gas window. Thus, depending on how the oil migrates, the distance over which the Elk Hills oils can migrate varies from $<$100 m to $\sim$500 km. For other fields where distances to the source rock are better constrained, this model may provide the means by which specific mechanisms of oil/gas migration can be distinguished. Efforts are currently underway to investigate such regions.

7. In summation

We conclude that Elk Hills production fluids contain a heavy noble gas enriched component of atmospheric origin that is indigenous to the hydrocarbons. This component was most likely adsorbed on and trapped in the carbon-rich source rocks [14–16] and subsequently mixed with the hydrocarbons during oil/gas generation and expulsion during the primary migration process. This initial hydrocarbon noble gas signature is diluted with noble gases extracted from ASW during secondary migration and reservoir storage. The effects of solubility fractionation of the noble gases (heavy gases more soluble than light gases in oil and in water) may provide a secondary mechanism which slows the efficiency of noble gas transfer from the ASW phase to the hydrocarbon phase making the calculated B ratio a slight underestimate if uncorrected for equilibrium processes. The extent to which the initial noble gas component is diluted places firm limits on the effective volume of water that has been in contact with the hydrocarbons, $B = \sim 6 - 80$ g$_{H_2O}$/g$_C$ for the Elk Hills field. We conclude that solution of methane and/or oil in water has had a limited role in the generation, migration and accumulation of oil in reservoirs of the Elk Hills

and, by inference, the North Sea [7]. We note that the B ratio of the Alberta gas fields [4] is of the order of 200–1000 g$_{H_2O}$/g$_C$ and that these gases occur with no accompanying oil phase. We cannot, therefore, rule out aqueous phase migration of methane in the Alberta system. However, the high water/methane ratios estimated for the Alberta field become a test for models describing basin scale hydrologic flow [26,27] by requiring geometries and oil–water contact times constrained by $B = 200–1000$ g$_{H_2O}$/g$_C$ over the lifetime of the reservoir.

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